MODIS Detached Coccolith Concentration Algorithm Theoretical Basis Document

Version 3

Submitted by

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Preface

This algorithm theoretical basis document (ATBD) describes the present state of development of the algorithm for retrieving the concentration of detached coccoliths from the coccolithophore *E. huxleyi* and from other coccolithophore species. It replaces Version 0 which was submitted on July 30, 1993, Version 1 submitted February 28, 1994, and Version 2 submitted November 1, 1994. Version 1 was peer reviewed in the spring of 1994 and reviewer suggestions were incorporated into Version 2. Version 3 incorporates the progress of studies relevant to the algorithm since Version 2 (in particular, see Section 3.1.2). The algorithm in its present form is ready for testing with SeaWiFS imagery. Experience gained with SeaWiFS imagery will be useful in assessing the performance of the algorithm.

1.0 Introduction

Coccolithophores are small marine Prymnesiophyte phytoplankton which form external CaCO₃ scales (diameter \sim a few μ m and thickness 250 to 750 nm) called coccoliths. The coccoliths can form multiple layers and eventually detach. Coccolithophores are the largest source of calcium carbonate on earth [Westbroek et al., 1985]. Of the coccolithophore species, Emiliania huxleyi is the most abundant, and its coccoliths can often be found from tropical to sub-arctic regions and further north into regions with water temperatures $< 0^{\circ}$ C [Heimdal, 1983]. The distribution of E. huxleyi coccoliths in sediments matches the distribution of the overlying species in the water column [McIntyre and Be, 1967]. Dissolution of calcite depends on the depth of the calcite compensation depth. Approximately 20% of the biogenic carbonate is lost before accumulation in the sediments in regions such as the Sargasso Sea [Fabry and Deuser, 1990], while 97% is lost in the Arabian Sea [Nair et al., 1989]. Even so, globally, calcium carbonate is responsible for about 75% of the deposition of carbon on the sea floor having a marine origin [Groom and Holligan, 1987; Honjo, 1986; Honjo, 1990], it and exceeds organic burial by a factor of seven. Thus, coccolith production is an important part of the biogenic carbon cycle.

2.0 Overview and Background

The importance of coccolithophores to the overall particulate pool of phytoplankton had not been realized until the advent of remote sensing. Upwelling radiance measurements from the CZCS frequently showed large, mesoscale features in the temperate waters of both hemispheres. These features were sometimes characterized by complete saturation of band 3 (550 nm wavelength) of the CZCS. They were later attributed to intense light scattering by coccolithophores and associated coccoliths [Holligan et al., 1983].

Perhaps the most intriguing aspect of coccolithophores concerns the frequency of their blooms. The archive of CZCS images shows alleged 100-200 km diameter coccolithophore blooms within temperate waters on an annual basis. Such blooms typically contain moderate to low chlorophyll concentrations so by inference, the organic carbon standing stock is low relative to the inorganic carbon. Blooms have been observed by satellite off of Argentina (Podesta unpublished data),

Northwest European Continental Shelf waters [Groom and Holligan, 1987; Holligan et al., 1983], the Gulf of Maine[Ackleson, Balch and Holligan, 1989], Scotian Shelf (Balch unpublished), Southern California Bight [Balch et al., 1989] and in the mid-Atlantic Bight and within warm-core rings [Blackwelder, 1984].

Apart from the inherent ecological interest in the development and fate of large-scale monospecific populations of phytoplankton, recent attention on the coccolithophores has focused on their role in global biogeochemical cycles. The flux of coccolith calcite to deep ocean water and sediments, which is known to have fluctuated in time [Bramlette, 1958; McIntyre and McIntyre, 1971], is recognized to be an important factor in determining the exchange of CO₂ between the oceans and the sediments [Dymond and Lyle, 1985; Sarmiento, Toggweiler and Najjar, 1988]. Over long time scales calcium carbonate is the major form in which carbon is buried in marine sediments [Whitfield and Watson, 1983], but in the short term the formation of calcite represents a source of CO₂ [Paasche, 1964] (but see Sikes and Fabry [1994]) due to the relationship

$$Ca^{+2} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O.$$

A further complication is that during warm climatic periods, including the present interglacial, rates of calcification in the oceans due to coccolithophores and other calcifying organisms [Berger, 1982; Bramlette, 1958; Hay and Southam, 1977] appear to be higher so that the above equation represents a potential positive feedback mechanism on levels of CO₂ in the atmosphere and, therefore, on global temperature.

These observations concerning coccolithophores: (1) their ubiquitous nature, (2) their possible role in climate, and (3) their intense scattering, make a global-scale study of their distribution an important application for MODIS imagery. We would ultimately like to estimate the rate at which CaCO₃ is formed by phytoplankton and look for long-term changes in that rate.

MODIS is ideal for such a study because of two unique characteristics: first its high radiometric sensitivity should, in principle, allow the detection of smaller quantities of coccoliths than CZCS; and second, the existence of the land bands on MODIS, e.g., band 3 and 4, with their high saturation radiance will enable study of very high concentrations of coccoliths that would saturate a typical ocean color instrument.

3.0 Algorithm Description

The algorithm for extracting the detached coccolith concentration from surface waters is based on the semianalytic model of ocean color of $Gordon\ et\ al.\ [1988]$. Briefly, the model relates the normalized water-leaving radiance $([L_w]_N)$, i.e., the radiance that would exit the ocean if the sun were at the zenith and the atmosphere were removed $[Gordon\ and\ Clark,\ 1981]$, to the absorption and scattering properties of the constituents of the water using radiative transfer theory. The absorption and scattering properties are then related to the constituent concentrations through statistical analysis of direct measurements. Therefore, they represent oceanic- or regional-averaged relationships. The model is validated by comparison with a set of $[L_w]_N$'s $[Clark,\ 1981]$ independent of the measurements used to establish the statistical relationships between constituents and optical properties.

3.1 Theoretical Description

In this section we first describe how the model is used to derive the detached coccolith algorithm. Next, we review the results of recent research, and discuss issues requiring further research. Finally, we discuss implementation of the algorithm, validation, and quality assurance.

3.1.1 Physics of the Algorithm

Unlike phytoplankton pigments, the presence of which decrease the radiance in the blue but increase it only slightly in the green, coccolithophore blooms tend to increase the radiance uniformly in both the blue and green [Gordon et al., 1988]. Thus, their remote study requires an understanding of the actual water-leaving radiance rather than just radiance ratios as in the case of pigments [Gordon and Morel, 1983]. Furthermore the "flattening" of the reflectance spectrum of coccolithophore blooms implies that the standard pigment algorithms [Gordon et al., 1983] will not provide correct pigment retrievals within the blooms. Gordon et al. [1988] have developed a prototype model for explaining the dependence of the water-leaving radiance on the concentration of constituents in Case 1 waters. This model provides the basis for extraction of the concentration of

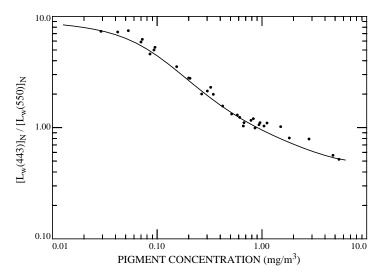


Figure 1. Variation in the $[L_w(440)]_N/[L_w(550)]_N$ with pigment concentration C. Points are Clark's [Clark, 1981] measurements and the solid line is the semi-analytic radiance model $[Gordon\ et\ al.,\ 1988]$ in the absence of coccolithophores.

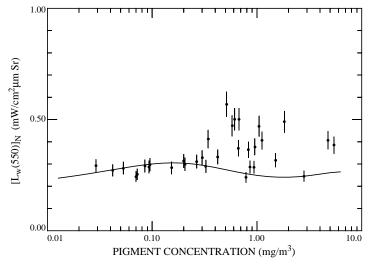


Figure 2. Variation in the $[L_w(550)]_N$ with pigment concentration C. Points are $\operatorname{Clark's}[\operatorname{Clark},\ 1981]$ measurements and the solid line is the semi-analytic radiance model $[\operatorname{Gordon}\ et\ al.,\ 1988]$ in the absence of coccolithophores.

the detached coccoliths of coccolithophores from the water-leaving radiance deduced from satellite imagery.

Briefly, the normalized water-leaving radiance is related to the absorption and scattering properties of the biogenic components of the water — phytoplankton and their associated detritus. The model is highly successful at explaining the dependence of the blue-green water-leaving radiance ratio on the pigment concentration (Figure 1). It is moderately successful at relating the actual radiances themselves to the pigment concentration. Figure 2 compares the computed and observed relationship between $[L_w(550)]_N$ and C. The "noise" in the relationship for $C > 0.3 \text{ mg/m}^3$ is interpreted as being due to the natural variation in the backscattering of plankton and detritus. In the figure the plankton-detritus scattering parameter has been adjusted to provide the "best fit" for $C < 0.3 \text{ mg/m}^3$. The resulting value is well within the range generally found for Case 1 waters $[Gordon\ and\ Morel,\ 1983]$.

It is straightforward to introduce detached coccoliths from coccolithophores into the model by simply including their contribution to the backscattering. By direct measurement of detached

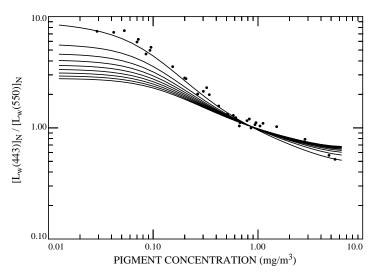


Figure 3. Variation in the $[L_w(440)]_N/[L_w(550)]_N$ with pigment concentration C. Points are Clark's [Clark, 1981] measurements and the solid line is the semi-analytic radiance model $[Gordon\ et\ al.,\ 1988]$. The coccolith concentration varies from 0 to 200×10^9 coccoliths/m³. The higher coccolith concentrations yield the "flatter" curves.

coccoliths in the Gulf of Maine, Balch et al. [1991] have shown that at 436 and 546 nm the backscattering coefficient $b_b(\lambda)$ of the detached coccoliths can be approximated by

$$b_b(\lambda) = A(\lambda)C_{cc},\tag{1}$$

where C_{cc} is the concentration of detached coccoliths, $A(436) \approx 1.5 \times 10^{-13} \text{ m}^2 \text{ coccoliths}^{-1}$, and $A(546) \approx 1.1 \times 10^{-13} \text{ m}^2 \text{ coccoliths}^{-1}$. Based on these measurements we approximate the spectral variation of $b_b(\lambda)$ by

$$b_b(\lambda) \propto \lambda^{-1.35}$$
. (2)

Figures 3 and 4 provide the radiance ratio and $[L_w(550)]_N$ as a function of C and C_{cc} as derived from the radiance model. Examination of these figures suggest that C_{cc} can be retrieved from $[L_w(550)]_N$ to within a factor of two simply by assuming that $C = 0.5 \text{ mg/m}^3$, e.g., if C = 0.5 ${\rm mg/m^3}$ and $C_{cc}=10^5~{\rm ml^{-1}}$, then assuming $C\approx 0.01~{\rm mg/m^3}$ yields $C_{cc}\approx 65\times 10^9~{\rm coccoliths/m^3}$, while assuming $C \approx 6 \text{ mg/m}^3$ yields $C_{cc} \approx 200 \times 10^9 \text{ coccoliths/m}^3$. However, given an estimate of C_{cc} , we can use Figure 3 to provide a reasonable estimate of C, which in turn can be used to improve the estimate of C_{cc} . In fact, if we can isolate C into specific ranges, i.e., C < 0.1, $0.1 < C < 0.3, \, 0.3 < C < 0.5, \, 0.5 < C < 1, \, 1 < C < 2, \, {
m and} \, \, C > 2 \, {
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m Figure} \, \, 3$ suggests can be done with little influence from the coccolith scattering, C_{cc} can be estimated with an error $\sim 10\text{-}20\%$. Note, however, that the basic relationship between b_b and C_{cc} , i.e., Eq. (1) is not established to this accuracy. The procedure is simplified by trying to estimate C and C_{cc} simultaneously from $[L_w(440)]_N$ and $[L_w(550)]_N$. A graphical scheme for effecting this based on the semi-analytical radiance model is provided in Figure 5. Examination of Figure 4 suggests that the natural variation in phytoplankton backscattering for $C < 10 \, \, \mathrm{mg/m^3}$ corresponds to a change in C_{cc} from 0 to 25×10^9 coccoliths/m³. Thus given accurate values of $[L_w(\lambda)]_N$, there will always be a 25×10^9 coccoliths/m³ uncertainty in C_{cc} with a CZCS-type instrument. Figure 5 suggests that the sensitivity of the radiances to C_{cc} falls by about a factor of two from high C to low C. Note that Figure 5 provides a simultaneous method for deriving both C_{cc} and C in coccolithophore blooms; however, the sensitivity to C for $C > 2 \text{ mg/m}^3$ is very poor. It forms the basis of the coccolith algorithm.

3.1.2 Recent Advances and Issues Requiring Further Study

3.1.2.1 Review of Coccolith Backscattering

The algorithm is based on Eqs. (1) and (2), which represents the scattering by detached coccoliths in the Gulf of Maine. It is a theoretical construct based on a model that appears to be

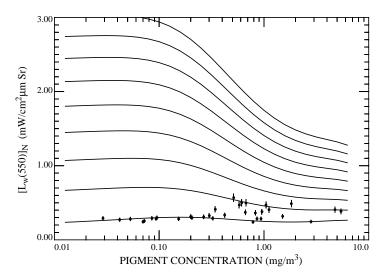


Figure 4. Variation in the $[L_w(550)]_N$ with pigment concentration C and the concentration of detached coccoliths. Points are Clark's [Clark, 1981] measurements and the solid line is the semi-analytic radiance model $[Gordon\ et\ al.,\ 1988]$. The coccolith concentration varies from 0 to 200×10^9 coccoliths/m³ from bottom to top.

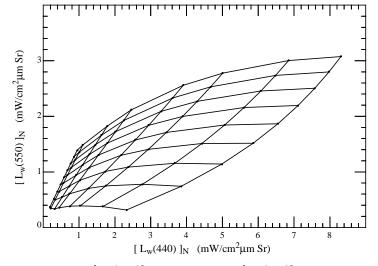


Figure 5. $[L_w(550)]_N$ as a function of $[L_w(440)]_N$ for various combinations of C and C_{cc} . The less sloped lines are lines of constant C_{cc} ranging from 0 (bottom) to 200×10^9 coccoliths/m³ (top) in steps of 25×10^9 coccoliths/m³. The more sloped lines are lines of constant C. The C-values are 0.03, 0.1, 0.2, 0.3, 0.6, 1, 2, and 6 mg/m³ from right to left.

valid for U.S. coastal and oceanic waters. At best the results are specific to this species and to the detached coccoliths. The yield of the algorithm (Figure 5) is the detached coccolith concentration (number m^{-3}). We need to determine if this algorithm is applicable to coccoliths produced by open ocean blooms of E. huxleyi and by other commonly found species of coccolithophores. Most importantly for biogeochemical models, we need to determine if we can tune the algorithm to yield the suspended calcite concentration of the water directly, rather than the concentration of coccoliths. We have ignored the scattering by intact cells, both naked and plated; however, Bricaud, Morel and Prieur [1983] have shown that the E. huxleyi cells themselves are very strong scatterers. Thus, we need to know the relative importance of the effect of plated cells, naked cells, and coccoliths on $[L_w(\lambda)]_N$, as cells misinterpreted as coccoliths may be a potential source of error. Experiments have already been initiated to determine the coccolith-specific scattering coefficients in culture as well as the effects of growth-phase on coccolith morphology and light scattering. Most of these results are in the dissertation of J. Fritz (U. Miami) and will be published in peer-reviewed journals.

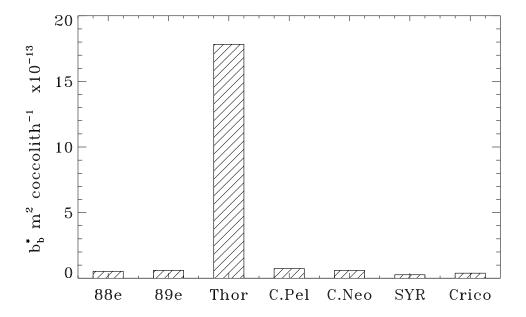


Figure 6. Total backscatter per calcite particle at 546 nm $[b_b^*; m^2]$ (Calcite particle)⁻¹] for several species of calicifying algae. In order from left to right: *Emiliania huxleyi*, strain 88e; *Emiliania huxleyi*, strain 89e; *Thoracosphaera sp.*; Coccolithus pelagicus; Coccolithus neohelis; Syracosphaera sp.; and Cricosphaera sp. Total variability is about 70 X between the various species.

Preliminary data has shown that the detachment rate of coccoliths from cells generally is the same as the growth rate. Thus, by documenting the rate of increase of detached coccoliths in the field, growth rate information about coccolithophores may also be acquired. To our knowledge, this is a unique opportunity for understanding the growth of an important primary producer based on satellite measurements. We have performed important preliminary experiments to measure the calcite-dependent scattering of coccoliths from various species. Basically, a flow cytometer

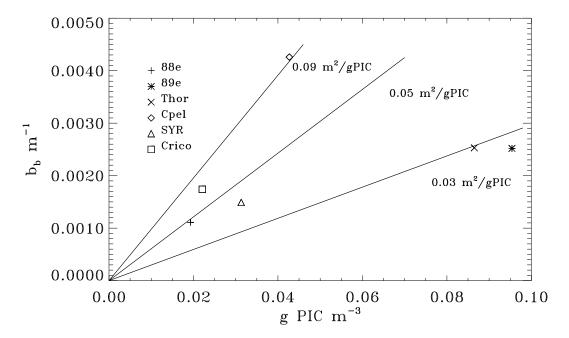


Figure 7. Acid labile backscatter at 546 nm $[b_b; m^{-1}]$ for several species of calicifying algae shown in Figure 6. Symbols are as follows: + *Emiliania huxleyi*, strain 88e; * *Emiliania huxleyi*, strain 89e; \times *Thoracosphaera sp.*; \diamond *Coccolithus pelagicus*; \triangle *Syracosphaera sp.*; and \square *Cricosphaera sp.* Slopes of the three lines represent the total variation in the calcite-specific backscatter which is about 3X.

was used to sort individual coccoliths and plated cells into filtered seawater. Then the volume scattering function was measured. We found that for seven species of calcifying algae, the coccolith-specific backscattering coefficient, b_b^* , the measured backscattering coefficient b_b divided by the concentration of coccoliths, varied by a factor of about 70 (Figure 6). We hypothesized that if backscattering coefficients of calcite covered cells were calculated per unit mass calcite, then the backscattering coefficient would be much less variable, regardless of species. Somewhat at odds with this hypothesis were the results of anomalous diffraction predictions for scattering by calcite spheres [Balch et al., 1996; van de Hulst, 1957]. These results suggested that the calcite-specific

scattering coefficient of calcite spheres should not be constant, but extremely size-dependent, with peak scattering efficiencies for 1-2 \(\mu\)m particles, the diameter of many coccoliths. Note, these anomalous diffraction calculations were for scattering, not backscattering, and there are reasons to expect differences in particulate backscattering properties and scattering properties as a function of size. For example, most of the light scattering in the ocean comes from particles $< 8 \mu m$ diameter while much of the backscattering is from particles < 1 μm [Stramski and Kiefer, 1991]. We found that the in earlier experiments with bulk cultures, that calcite-specific b_b^* of plated coccolithophores had low variance, only varying a factor of 3 across the species examined (Figure 7), contrary to the anomalous diffraction predictions for b^* . The limitation of these experiments were that we only could use size fractionated cells from bulk cultures, and those cells contained both particulate inorganic carbon (as calcite) and particulate organic carbon; they did not contain pure calcite. Moreover, the flow cytometer still could not sort non-fluorescing, scattering coccoliths, free from organic matter. This was because we had no distinct "tag" that we could use to separate coccoliths from other non-fluorescent detritus. The problem of mixing organic and inorganic carbon became particularly acute in our measurements of the calcifying dinoflagellate Thoracosphaera sp., in which the presence of cellular protoplasm in the calcite thecae significantly altered the scattering coefficient of the whole particle. The issue that we faced in subsequent experiments was to measure the calcitespecific backscattering coefficient for pure biogenic calcite particles, free of cells. Therefore, we set out to design the definitive experiment in which we used a flow cytometer to sort pure coccolith suspensions, after which light scattering was examined. This required major enhancements of our analytical abilities, both in flow cytometry and in calcite detection.

3.1.2.2 Recent Laboratory Experiments

We ran a series of flow cytometer experiments at Bigelow Laboratory in late 1995. The goal of the experiments was to sort individual coccoliths with the flow cytometer, to measure the volume scattering properties of the sorts, then to measure the mass of calcite within the sort. Sorting of individual coccoliths is not trivial with the flow cytometer due to their small size and lack of autofluorescence, and it required careful tuning of the instrument so that we could sort coccoliths based on their birefringence (i.e., the ratio of horizontally- and vertically-polarized forward light scattering). Moreover, this work required much more precise measurements of calcium concentration, than heretofore made on these calcifying algal species. This was particularly difficult when one considers that seawater (and flow cytometer sheath fluid) has Ca⁺⁺ concentrations in

excess of 10 μ M. Fortunately, we have access to a graphite furnace atomic absorption spectrometer, with three orders of magnitude more sensitivity (50 pg Ca ml⁻¹) than flame atomic absorption. The instrument, a Perkin Elmer Model 5100PC, belongs to Dr. Larry Mayer at the Darling Center, University of Maine (Walpole, ME). Our technician took the Perkin Elmer course in Atlanta, GA in order to process the samples. As an example of the experiments, we sorted 100,000 coccoliths of *Emiliania huxleyi* (2 μ m diameter) with the flow cytometer. This translated to 25 ng C or 83 ng Ca, which, in a 5 mL final volume, gave a concentration of 16.6 ng Ca ml⁻¹ (still sufficient to give a signal to noise ratio > 300 on the graphite furnace atomic absorption spectrometer).

Species of calcifying algae (both coccolithophores and Thoracosphaera heimii, the calcifying dinoflagellate) were purchased from the Provasoli-Guillard Culture Collection (at Bigelow Laboratory), and grown in K media. Cultures were kept in the temperature-controlled rooms at Bigelow on a 14h:10h light:dark cycle and harvested in logarithmic growth phase for sorting with the EPICS V flow cytometer with multi-parameter data acquisition. Calcite particles then were sorted based on their birefringence under the laser light. Polarizing filters were placed, at right angles, on the two forward-angle scatter detectors of the flow cytometer[Olson, Zettler and Anderson, 1989]. Olson showed that the ratio of horizontally to vertically polarized forward light scatter was about 3 for calcite particles and 1 for all other particle types (we have found a ratio closer to 12 for coccoliths using the Bigelow Laboratory flow cytometer). This proved highly effective for discriminating and sorting calcite particles.

We performed the necessary set-up, cell counts and cell sorting for five calcifying algal species (which required that we started our culturing activities at least 2.5 weeks prior to the beginning of the experiment). Two species, Syracosphaera sp. and Coccolithus pelagicus grew in clumps which caused problems in sorting individual coccoliths. The other three species, E. huxleyi (clone 89E), Cricosphaera sp., and Thoracosphaera sp. were adequate for our experiments. We spent two days of our week of flow cytometer time tuning the flow cytometer for sorting individual coccoliths and verifying that flow cytometer counts versus regular cell counts were in good agreement. This was absolutely critical to our final results. One aspect that allowed this work to proceed more rapidly than previous experiments, however, was that there was no need to sort plated cells since the goal was to define the backscattering coefficient per mg of calcite carbon. We calibrated our laser light scattering photometer using an isotropic scattering standard supplied with the instrument, and frequently checked for any instrument drift with ultra-clean distilled water.

The results showed that, indeed, the coccolith-specific backscattering coefficients were highly variable as indicated by the differences in slopes of the lines in Figure 8. All comparisons of

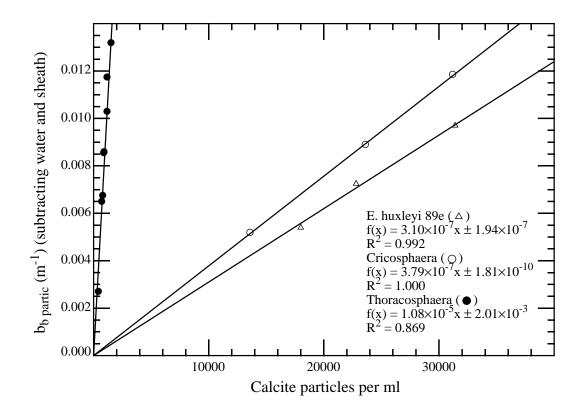


Figure 8. Particulate backscattering versus numbers of calcite particles for *E. huxleyi* coccoliths (open triangles), *Cricosphaera* coccoliths (closed circles) and empty thecae of *Thoracosphaera sp.* (open circles). Concentrations of calcite particles based on light microscope counts.

 b_b particulate versus the concentration of Ca are shown in Figure 9 and demonstrate much less variance than the coccolith-specific values (Figure 6). The best-fit average calcite-specific b_b^* value for these data was 11.7 m² (mol Ca)⁻¹, with a standard deviation of ± 3.2 m² (mol Ca)⁻¹. This average b_b^* is indicated with the line on Figure 9. Equally noteworthy, is the fact that the calcite-specific b_b^* based on pure sorts of coccoliths was about an order of magnitude higher than the values based on plated cells (which contained both organic and inorganic matter). Our previous results in which plated coccolithophores were sorted gave calcite-specific b_b^* values averaging about 0.6 m² (mol Ca)⁻¹ with a standard deviation of 0.36 m² (mol Ca)⁻¹ (Figure 7). The presence of absorbing organic matter obviously reduced the quantity of scattered light detected by the

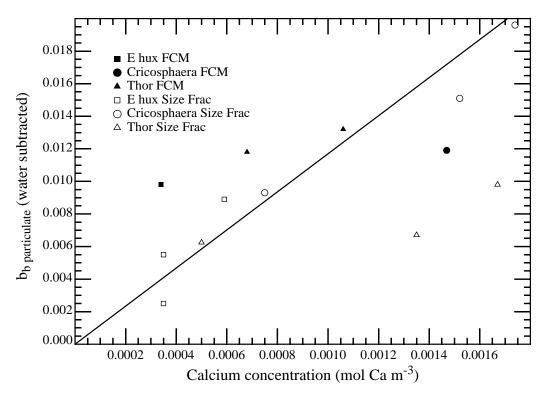


Figure 9. Particulate backscattering versus concentration of suspended calcite (mol m⁻³). Solid symbols are from flow cytometer experiments. Open symbols are from size fractionation experiments. Species represented are: $Emiliania\ huxleyi$ (squares), $Cricosphaera\ sp.$ (circles) and Thoracosphaera (triangles). Line represents average b_b^* for all species of 11.7 m² (mol Ca)⁻¹. Standard deviation of this line is ± 3.2 m² (mol Ca)⁻¹.

scatterometer. Such an observation only serves to emphasize the importance of preparing pure coccolith suspensions in order to determine their b_h^* .

The confirmation of low variance in the calcite-specific b_b^* for a wide range of particle sizes has significant ramifications for the remote sensing of suspended calcite. Simply put, the results suggest that for remote reflectance measurements of calcite, one need not know the species (particle type) responsible in order to calculate the suspended load of calcite with an uncertainty of about 25%. If our results had shown more species-specific variance in b_b^* , then one would have had to know the type of particle in order to calculate the amount of suspended calcite. Moreover, our results showed that b_b^* values were less size dependent than the b^* values (predicted from anomalous diffraction calculations on calcite spheres).

We now are performing the last phase of this work, in which we will sort natural calcite particles sampled from ships of opportunity from the world oceans. These samples will be sorted using the polarizing filters placed at right angles over the two forward-angle scatter detectors of the flow cytometer. This will provide a more representative estimate of the backscattering coefficient for naturally-occurring calcite particles.

3.1.2.3 Recent Field Experiments

For obtaining field data on calcite-dependent backscattering, we have developed a secondgeneration underway scattering system. It uses a Wyatt Technologies laser-light scattering photometer equipped with a flow-through cell to measure volume scatter at 18 angles. Integration of this signal in the backward direction allows us to calculate backscatter in real time. This last year, we performed considerable programing and instrument interfacing in order to streamline the data flow. The system now monitors chlorophyll fluorescence, pH, temperature, salinity and 18-channel volume scatter. A Global Positioning System was interfaced, as well. In January 1995, we took our flow-through light scattering detector to sea for its first field trials. Despite some very rough seas, the instrument ran without problem, and we recovered four detailed transects across the Florida Straits for volume scattering (sampling at 400 per second, and averaging over 3-5 minute time intervals). These average volume scattering functions were used to calculate the backscattering coefficients on the same time scale. Given the velocity of the ship, this translated to horizontal resolution of about 900 m. (This can be shortened to 300 m resolution with no problem). While returning to Miami, we scaled 3 orders of magnitude in b_b , most of it resulting from calcite particles being resuspended and sloughing off the carbonate banks of the SE Florida shelf. Such high concentrations of suspended calcite are similar to the most dense coccolithophore blooms that we have ever visited; this raises interesting questions about the importance of suspended calcite to overall light scatter in Case 2 waters near carbonate banks.

In October and November, we took the underway flow-through system to the Arabian Sea for a 35 day cruise during the intermonsoon period. The instrument ran virtually flawlessly, and we collected continuous data of total backscattering and calcite-dependent backscattering over the 3500 km cruise track. Interestingly, we demonstrated that consistently 10-30% of the total backscattering in the Arabian Sea was acid-labile (i.e., originated from calcite). The instrument also logged statistics of the backscattering events every 4 minutes of the trip. The data showed that

various water masses could be characterized by well-defined scattering statistics (e.g., a striking relationship between the standard deviation of the scattering events, and the average backscattering value was found, suggesting a changing role of rare, large scatterers in certain water masses over the cruise track).

Relatively speaking, the Arabian Sea is not a region known for meso-scale coccolithophore blooms. In March and June of 1996, we had an opportunity to take the flow-through instrument into the Gulf of Maine where the coccolithophore, Emiliania huxleyi forms large blooms. As expected, calcite-dependent backscattering was low in March, but it was still measurable. In June, we ran 2000 miles of transect in the Gulf of Maine with our flow-through light scattering photometer and may have observed the early stages of coccolithophore bloom development in Wilkinson Basin. Acid-labile scatter dropped over Georges Bank, and increased in the Northeast Channel, similar to previous blooms that we have observed. The observations are consistent with the calcite being produced in the more stable Wilkinson Basin with subsequent advection around the NE flank of Georges Bank. We are preparing for another Gulf of Maine cruise at the end of October and, again, will be taking the flow-through system.

3.1.2.4 Issues Requiring Further Study

Clearly an issue that requires further study is confirmation that naturally-occurring calcite particles in the sea have the same calcite-specific scattering properties as the calcite particles formed by cultured calcifying algae. We are holding preserved samples collected worldwide from ships of opportunity. We intend to sort these calcite particles into particle-free water, measure the volume scattering function as well as the calcite concentration.

Another issue relates to validation of the algorithm in both the pre- and post-launch phases. We will be performing more sea-truth measurements to compare (a) the coccolith concentration, (b) the calcite concentration, and (c) the relevant inherent and apparent optical properties — backscattering, scattering (as determined by beam attenuation- absorption), water-leaving radiance, downwelling irradiance, and diffuse reflectance — to predictions by the algorithm, i.e., given $[L_w]_N$ at 440 and 550 nm, does the algorithm predict the correct value of the coccolith and calcite concentrations?

3.1.3 Mathematical Description

The algorithm as presently configured consists of a set of lookup tables providing information similar to Figure 5. However, there may have to be sets that are specific to particular regions (because of speciation variations) and to latitude belts. Mitchell [1992] has shown that the chlorophyll-specific absorption coefficient of particulate matter in the polar regions is significantly lower than in the temperate oceans. Thus, application of the algorithm to polar regions would require the Gordon et al. [1988] model be modified to reflect this fact. In fact, there may be a range of chlorophyll-specific absorption coefficients [Carder et al., 1991] requiring region-specific algorithms. Also, to the extent that a single species of coccolithophore dominates intense blooms in certain regions, e.g., E. huxleyi in the North Atlantic or Umbilicosphaera sibogae in the California Current [Balch et al., 1989], it may be necessary to have species-dependent algorithms for particular regions and times. This would require species-dependent versions of Eqs. (1) and (2); however, in the case of the more-meaningful calcite concentration, the species-dependent variations are significantly smaller (Figure 9).

3.1.4 Uncertainty Estimates

Since the algorithm uses absolute values of the water-leaving radiances, it is more susceptible to errors in atmospheric correction than algorithms employing radiance ratios. Thus, atmospheric correction can be an important source of error over and above the inherent error in the algorithm due to natural variability. It is possible to understand the effects atmospheric correction errors on C_{cc} in a simple manner. If the atmospheric correction is in error by ± 0.001 in reflectance $(\pi L/F_0\cos\theta_0)$, where L is the radiance, F_0 is the extraterrestrial solar irradiance, and θ_0 is the solar zenith angle), the error in the radiance will be approximately ± 0.06 mW/cm² μ m Sr in each band for small θ_0 . From this we can use Figure 5 to ascertain that the error due to atmospheric correction will be small $\Delta C_{cc} < \pm 5 \times 10^9$ coccoliths/m³ for low C and C

Another potential source of error is derived from the fact that the atmospheric correction algorithm assumes that $[L_w(\lambda)]_N = 0$ for $\lambda = 765$ and 865 nm, i.e., in the near infrared (NIR). For sufficiently high coccolith concentrations this will be violated which will degrade the atmospheric correction and therefore the retrieval of $[L_w(\lambda)]_N$ in the blue and green, introducing more uncertainty in C_{cc} . In order to estimate the seriousness of this problem, scattering (or normalized water-leaving radiance) data is required in the NIR. Such data are not available. However, if one assumes that Eq. (2) is valid into the NIR, then for $C_{cc} = 100 \times 10^9$ coccoliths/m³, the error (bias) introduced into $[L_w(\lambda)]_N$ in the blue-green is about $-0.2 \text{ mW/cm}^2 \mu \text{m}$ Sr, or about one small scale division on the axes of Figure 5.

3.2 Practical Considerations

We believe that the lookup table approach described above is optimum, and this is our working hypothesis. Significant modification or an entirely different approach may be required for the final algorithm, e.g., it might be necessary to analytically derive $b'_{cc}(\lambda)$ using the radiance model and then derive C_{cc} using Eq. (1). It is too early to speculate on some portions of the individual subsections below and parts are occasionally marked "TBD" (To Be Determined). Please note that those that are not marked TBD are not necessarily complete.

3.2.1 Validation

The validation of the C_{cc} and calcite concentration products will be effected by comparing simultaneous surface-based measurements and MODIS-derived values. This will be effected in the pre-launch phase by utilizing ship data, i.e., comparing products derived from measurements of $[L_w]_N$ with those measured directly, as well as data from other ocean color sensors (SeaWiFS, OCTS, etc.) if available. In the post-launch phase, we shall participate in the MODIS Ocean Group validation effort (see Science Data Validation Plan, MODIS Oceans Group, available on World Wide Web at html://spso.gsfc.nasa.gov/validation/docs.html); however, we shall also carry out a validation effort specifically focused on coccoliths. For this, station locations will be chosen to provide a wide range of values; however, it will be centered on intense blooms. An experimental method will be developed to enable the estimation of the influence of subpixel structure.

3.2.2 Quality Control and Diagnostics

If our assumptions are valid the algorithm can be expected to perform properly unless $[L_w(550)]_N$ is too small or too large (specific values are TBD). To insure that the algorithm results are of the highest quality, we will check the output relative to expected ranges. Output which falls beyond specified confidence limits will be flagged. For example, typical suspended calcite concentrations in the blue ocean fall between 0-1 μ mol CaCO₃ per liter (a recent trip to the Equatorial Pacific showed concentrations of 0.2-0.3 over much of the Equatorial region). Values of 4 and 5 μ mol CaCO₃ liter are easily found in the North Atlantic in summer but otherwise would be considered high. Blooms of coccolithophores will be characterized by calcite concentrations of 30-40 μ mol CaCO₃ per liter. Higher suspended calcite concentrations in the sea have been observed before only in the rarest circumstances and output exceeding this concentration should be flagged (note, this is equivalent to E. huxleyi coccolith concentration of about 1.6 million coccoliths per ml!). At the minimum, this would probably allow us to differentiate when the high reflectance was due to coccolithophores or some other high-reflectance algae which is concentrated at the surface, e.g., Trichodesmium. Over the course of the mission, statistics will be developed with which algorithm results can be compared to previous determinations.

Another error that needs to be continuously monitored relates to the look-up table shown in Figure 5. Recall that as chlorophyll concentrations increase, the isopleths of chlorophyll are closer and closer together. In other words, a 10% error in $L_w(440)$ at low chlorophyll concentrations may only mean an absolute error of 0.01 μ g Chl per liter, whereas the same error at low radiance values (high chlorophyll) will cause an error of 4 μ g Chl per liter. The current version of the algorithm is least accurate at high chlorophyll concentrations, and values over about 5 μ g Chl per liter should be flagged, whether calcite concentrations are high or low.

3.2.3 Exception Handling

Exceptions occasionally occur in a manner that prevents operation of the algorithm, e.g., missing data in bands the required bands near 440 and 550 nm, or data that fall outside the range of "reasonable" values. A series of flags will be developed to indicate when the retrievals should not be attempted.

3.2.4 Data Dependencies

At this time, only $[L_w(443)]_N$ and $[L_w(550)]_N$ are expected to be needed; however, for quality assurance procedures, it will be necessary to have a low spatial resolution, global scale, time series of retrievals to signal the appearance of large unexpected changes in the output products. Assembly of this set will be effected along with similar sets for other MODIS ocean products collectively by the MODIS Oceans Group.

3.2.5 Output Products

The output products will be C_{cc} , an estimate of the calcite concentration, C, a descriptor of the particular lookup table(s) used, and a quality measure based on the value of $[L_w(550)]_N$. If $[L_w(550)]_N$ is too low or too high (specific values are TBD), the algorithm may return poor results which will be indicated by the quality measure for each retrieved variable.

4.0 Assumptions and Constraints

In this section we describe the assumptions that have been made and how they may influence the resulting C_{cc} and C. We also provide scenarios for which the algorithm should not be used, and for which the returned value of C should be used in place of the standard ratio algorithm.

4.1 Assumptions

There are three main assumptions in this algorithm: (1) Eq. (1) is correct; (2) Eq. (2) is correct; and (3) the parameters in the radiance model are correct. Errors in these, and in particular the applicability of Eq. (1) and (2) on a global scale, will map to errors in the final product. One goal of our pre-launch field research is to provide an estimation of this mapping.

4.2 Constraints

The principle constraint is that the algorithm should only be used when $[L_w(550)]_N$ exceeds a given value (specific value is TBD). This value is above the range of the natural variation in $[L_w(550)]_N$ for a given C caused by variation in phytoplankton and associated detritus optical properties in the absence of coccoliths. Above this limit, the algorithm could be used to provide

an estimate of C, which may be better than the estimate provided by the ratio algorithms in coccolithophore blooms. If $[L_w(550)]_N$ becomes too large (specific value is value TBD) the algorithm should not be used because atmospheric correction will be too strongly influenced by the presence of the coccoliths.

5.0 References

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